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THE POLYMERIZATION OF NIBR₂(P(CH₂CH₂CN)₃)₂: A 'TRIPLY-SPECIFIC'--ETC(U)

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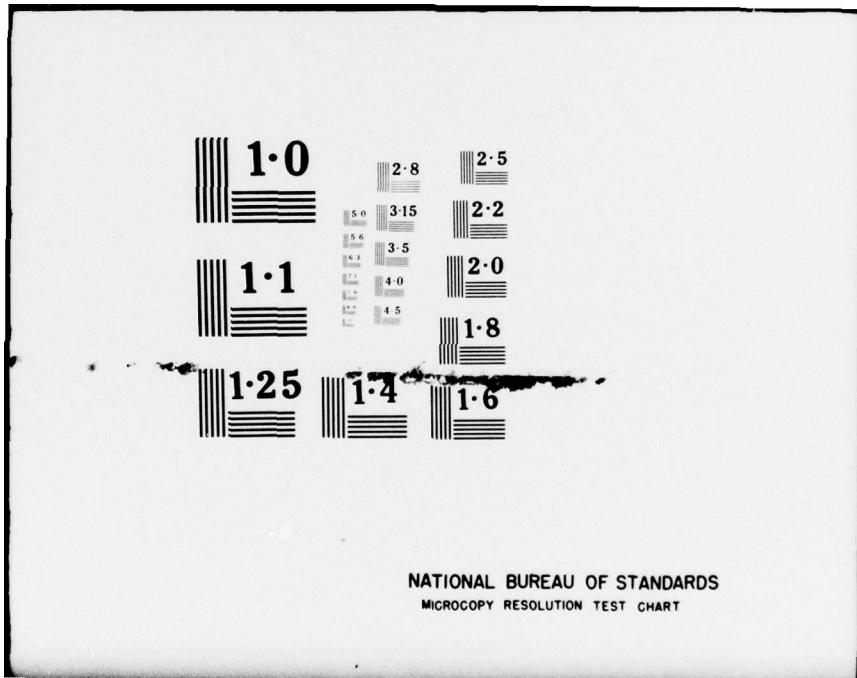
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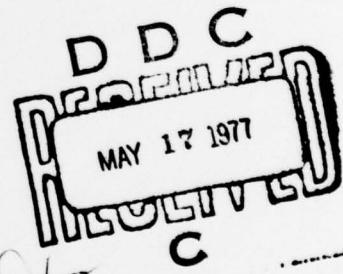
The Polymerization of $\text{NiBr}_2[\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3]_2$:
A "Triply-Specific" Solid State Reaction

Kent Cheng and Bruce M. Foxman

Department of Chemistry

Brandeis University

Waltham, Massachusetts 02154



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Contribution from the
Department of Chemistry,
Brandeis University
Waltham, Massachusetts 02154

The Polymerization of $\text{NiBr}_2[\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3]_2$:

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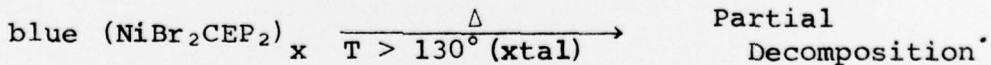
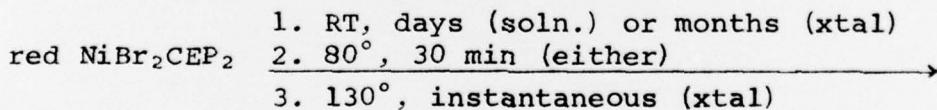
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Kent Cheng and Bruce M. Foxman*

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Sir:

The reactivity of coordination complexes in the solid state has been little explored.¹ Because of the rather stringent directional requirements, the most interesting solid-state reactions of coordination complexes are undoubtedly polymerization processes.² Studies of the potentially topochemical polyreactions of monomeric coordination complexes, by analogy with other inorganic and organic systems³ can thus lead to an understanding of synthetic, dimensional and symmetry-based criteria for the solid-state preparation of crystalline coordination polymers. Square-planar, red monomeric complexes of the type NiX_2CEP_2 ($\text{X} = \text{Cl}, \text{Br}$; $\text{CEP} = \text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$) are obtained as kinetic products at room temperature, and have been shown to undergo polymerization reactions in solution or in the solid state⁴ to yield highly crystalline, blue, octahedral coordination polymers. For $\text{NiBr}_2\text{CEP}_2$,^{4a} we have examined the polymerization in solution and in single crystals:



Further, we find that the reaction is characterized by (a) product specificity, (b) stereospecificity, leading to formation of linear polymer, (c) "crystallographic specificity" and (d) highly anisotropic "front motion" through individual single crystals.

When either an acetone solution or moist individual single crystals of monomer are allowed to polymerize at various temperatures, the blue polymeric product is always contaminated with a green material, which has defied characterization.⁵ However, when dry individual single crystals are allowed to polymerize at temperatures below $\sim 130^\circ$, only the blue polymeric product is formed. Thus, this reaction is readily product-specific only in the solid state. While the rate of polymerization is slower ($\sim \frac{1}{6}$) in the solid state at room temperature and below, the rates are about equal at 80° C, and the solid state transformation is faster above the latter temperature.

In order to determine the probable geometrical course of the reaction, we have carried out complete three-dimensional X-ray structure analyses on single crystals of monomer and polymer grown from solution:

Monomer, Orthorhombic, Pbca $\xrightarrow{}$ Polymer, Monoclinic, B2₁/c
 $a = 13.169, b = 22.004, c = 8.487 \text{ \AA}$ $a = 13.907, b = 21.055, c = 8.496 \text{ \AA};$
 $V = 2459.3 \text{ \AA}^3$ $\beta = 97.46^\circ; V = 2466.7 \text{ \AA}^3$

In both the monomer and polymer phases, Ni atoms occupy the centers of symmetry (0,0,0), ($\frac{1}{2}, 0, \frac{1}{2}$), ($0, \frac{1}{2}, \frac{1}{2}$), ($\frac{1}{2}, \frac{1}{2}, 0$). The crystal structure of the product phase shows that only Ni complexes at (0,0,0) and ($\frac{1}{2}, 0, \frac{1}{2}$) have reacted to form part of a repeating polymer chain, while Ni complexes at ($\frac{1}{2}, \frac{1}{2}, 0$) and ($1, \frac{1}{2}, \frac{1}{2}$) have reacted to form a

second polymer chain. This is a significant observation: since it can be shown that the solid-state reaction pathway is likely to be identical to that suggested by this "before and after" view (vide infra), we conclude that polymerization occurs only in specific ac planes in the crystal. Such a "layer-by-layer" reaction precludes cross-linking of polymer chains and may be expected to lead to the formation of rigorously linear polymer, as well as highly oriented crystalline product.

At temperatures $> 20^\circ$ the crystals do not show well-defined front motion as the reaction proceeds, hence we have confined our initial studies of reacting crystals to temperatures near -5° . Crystals of the monomer are well-defined, wine-red, nearly opaque prisms, elongated along [001], with well-defined {010}, {100}, (111), ($\bar{1}\bar{1}\bar{1}$), ($\bar{1}\bar{1}\bar{1}$), and ($\bar{1}\bar{1}\bar{1}$) faces. Reaction always begins on a single (100) face or on a pair of (100) faces; the reaction proceeds (over a 6-month period), with the first significant observation being a thin blue coloration of the entire (100) face. A very distinct blue reaction front then moves across the crystal, virtually parallel to the (100) face. X-ray diffraction studies of partially reacted crystals (5%-60% complete) show that the reaction is topotactic,⁷ and, further, that ($\overset{*}{a}_{\text{reactant}}$, $\overset{*}{a}_{\text{product}}$) and ($\overset{*}{b}_{\text{reactant}}$, $\overset{*}{b}_{\text{product}}$) are aligned. The c axis in the monoclinic product lies $\sim 7.5^\circ$ away from the $\overset{*}{c}$ axis of the reactant phase (note that in the transformation from orthorhombic to monoclinic,

β changes from 90° to 97.5°). However, for crystals where the solid-state reaction begins on a single (100) face, only one new ^{*} c axis is observed, i.e. twinning about [001] reactant does not occur to a detectable extent. Thus, the first product which appears on a crystal face appears to determine, in a crystallographically specific manner, unit cell orientation in the product. We note that this strictly linear polymerization process appears to be different from other carefully-studied examples,³ (including the polymerization of $\text{NiCl}_2\text{CEP}_2$),⁸ in which the polymer appears first in a solid solution with monomer, and crystallization/orientation of product may be effected via annealing.

The relationship between pairs of reactant and product molecules, chosen so as to be representative of the overall polymerization reaction, is presented in the Figure, which demonstrates the spatial similarities between reactant and product. The reaction mechanism qualitatively involves polymerization in crystal ac planes, followed by repacking of the polymer along the b direction; further, it may be shown that motion of the centroids of the individual complexes during reaction defines the product a axis (and β angle of 97.5°). The direction of slowest front motion (i.e. along the a direction) is consistent with the observation that only the a axis of the reactant crystal must reorient to form the product pseudomorph.

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5. The material is probably NiBr_2CEP (ref. 4a); it crystallizes in a trilled orthorhombic unit cell, and our structure analysis is as yet incomplete.

6. Coordinates: $\pm (x, y, z)$; $\pm (x, \frac{1}{2}-y, \frac{1}{2}+z)$; $\pm (\frac{1}{2}+x, y, \frac{1}{2}+z)$; $\pm (\frac{1}{2}+x, \frac{1}{2}-y, z)$.

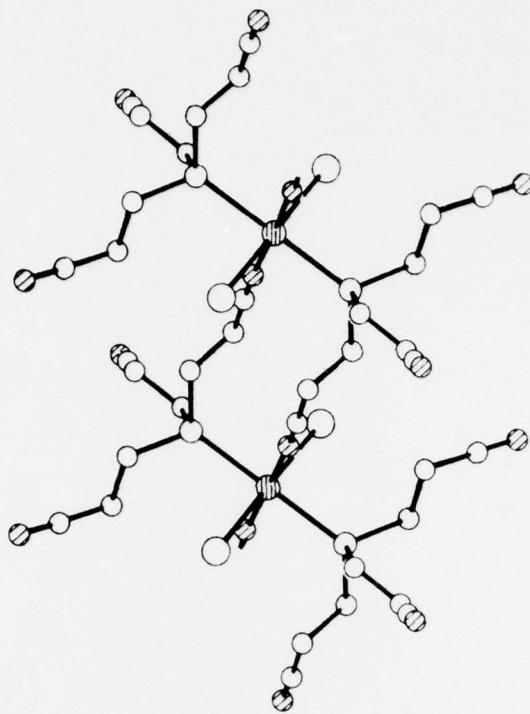
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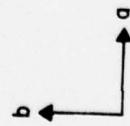
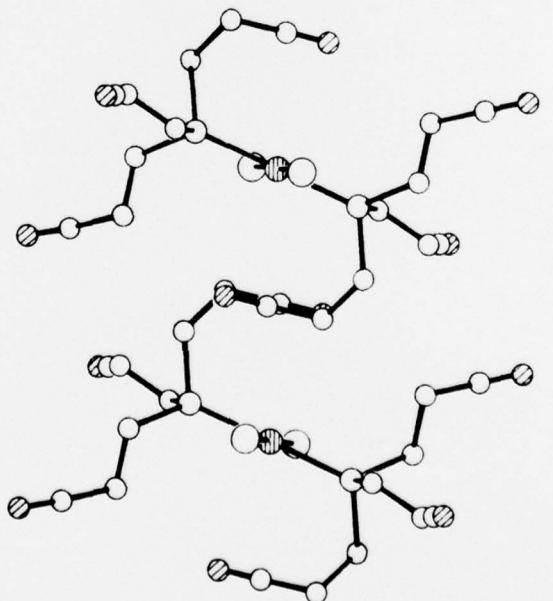
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Figure Caption

Figure 1. Pairs of reactant and product molecules viewed normal to the ab plane of the respective unit cells. Reaction front motion is slowest in the a direction.



○ N
○ C
○ P
○ Ni
○ Br



Abstract

The solid-state reaction of square-planar $\text{NiBr}_2[\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3]_2$ has been shown to lead to highly oriented crystals of octahedral polymer. Reaction of the monomer in the solid-state at -5° leads to product which is characterized by (a) freedom from the usual contaminants arising from reaction in solution; (b) stereospecificity, leading to formation of strictly linear polymer; and (c) topotaxy, in which ($\overset{*}{\text{a}}$ reactant, $\overset{*}{\text{a}}$ product), ($\overset{*}{\text{b}}$ reactant, $\overset{*}{\text{b}}$ product) are aligned for the orthorhombic reactant and monoclinic product phases; further, no twinning is observable in the product. There is a negligible volume change involved in the polymerization ($\sim 0.3\%$). Individual single crystals react at -5° with a well-defined front passing across the crystal, virtually parallel to a (100) face. This is consistent with the observation that only the a axis of the reactant crystal must reorient to form the product pseudomorph.

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